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REC'D 22 JUL 2004

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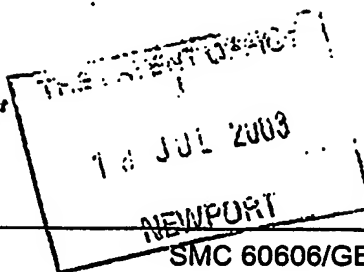
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The Patent Office

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1. Your reference

SMC 60606/GB/P1

2. Patent application number

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0316854.9

18 JUL 2003

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Avecia Limited  
Hexagon House  
Blackley  
Manchester, M9 8ZS  
United Kingdom

Patents ADP number (if you know it)

07764137001

If the applicant is a corporate body, give the country/state of its incorporation

GB

4. Title of the invention

Compounds, Inks and Processes

5. Name of your agent (if you have one)

MORPETH, Fraser Forrest

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Avecia Limited  
Hexagon House  
Blackley  
Manchester, M9 8ZS  
United Kingdom

Patents ADP number (if you know it)

07764137001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
  - b) there is an inventor who is not named as an applicant, or
  - c) any named applicant is a corporate body.
- See note (d))

# Patents Form 1/77

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Continuation sheets of this form

Description	16
Claim(s)	04
Abstract	01
Drawing(s)	

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature

C. Shepherd

Date 17/1/03

Avecia Limited Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

Mrs K.M. Pinder/Mrs G. Shepherd 0161 721 1361/2

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APPLICANTS

AVECIA LIMITED

TITLE

COMPOUNDS, INKS AND PROCESSES

COMPOUNDS, INKS AND PROCESSES

This invention relates to compositions, to compounds, to printing processes, to printed substrates and to ink-jet printer cartridges.

Ink-jet printing is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate. The set of inks used in this technique typically comprise yellow, magenta, cyan and black inks.

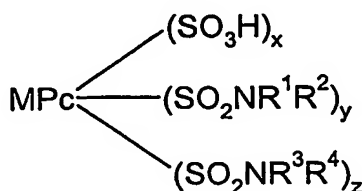
With the advent of high-resolution digital cameras and ink-jet printers it is becoming increasingly common to print off photographs using an ink-jet printer. This avoids the expense of conventional silver halide photography and provides a print quickly without the need to post a film to a developing service and wait days or weeks for it to be developed and returned.

While ink-jet printers have many advantages over other forms of printing and image development there are still technical challenges to be addressed. For example, there are the contradictory requirements of providing ink colorants that are soluble in the ink medium and yet do not run or smudge excessively when printed on paper. The inks need to dry quickly to avoid sheets sticking together after they have been printed, but they should not form a crust over the tiny nozzle used in the printer. Storage stability is also important to avoid particle formation that could block the tiny nozzles used in the printer. Furthermore, the resultant images desirably do not fade rapidly on exposure to light or common oxidising gases such as ozone.

Most cyan colorants used in ink-jet printing are based on phthalocyanines and problems of fading and shade change on contact with ozone are particularly acute with dyes of this class especially when they are printed onto media containing inorganic particles, e.g. silica and/or alumina. There appears to be some aspect of the environment on the surface of such media (particularly media used for photo-realistic ink-jet printing) that promotes deterioration of these dyes in the presence of ozone.

Thus, the present invention provides a composition comprising:

(a) a mixture of copper phthalocyanine dyes of Formula (1) and salts thereof:



Formula (1)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus;

R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> independently are H or optionally substituted C<sub>1-4</sub>alkyl;

R<sup>4</sup> is optionally substituted hydrocarbyl; or

R<sup>3</sup> and R<sup>4</sup> together with the nitrogen atom to which they are attached represent an optionally substituted aliphatic or aromatic ring system;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

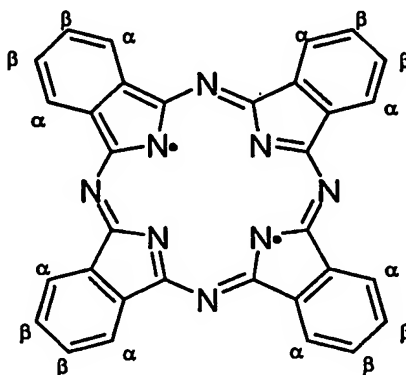
z is 0.1 to 3.8;

the sum of (x+y+z) is 4; and

the substituents, represented by x, y and z, are attached only to a β-position on the phthalocyanine ring; and

(b) a medium which comprises water and an organic solvent or an organic solvent free from water.

The phthalocyanine nucleus may be represented by the bivalent radical of formula:



When a dye of Formula (1) is made by the more usual route of sulfonating a phthalocyanine pigment followed by chlorination and then amination/amidation the resultant product carries sulfo and sulfonamide substituents in any susceptible position.

The copper phthalocyanine dyes of Formula (1) where the sulfo and sulfonamide substituents are attached to a β position on the phthalocyanine ring may be prepared by any method known in the art, and particularly by cyclisation of appropriate β substituted phthalic acid, phthalonitrile, iminoisoindoline, phthalic anhydride, phthalimide or phthalamide in the presence of a suitable copper or nickel salt, such as CuCl<sub>2</sub>, followed by chlorination and then amination/amidation.

Preferably copper phthalocyanine dyes of Formula (1) where the sulfo and sulfonamide substituents are attached to a β-position on the phthalocyanine ring are prepared by cyclisation of 4-sulfo-phthalic acid, in the presence of a suitable copper or nickel salt such as CuCl<sub>2</sub>, to phthalocyanine tetrasulfonic acid. The phthalocyanine tetrasulfonic acid is then chlorinated and the sulfonyl chloride groups so formed are reacted with compounds of formula HNR<sup>1</sup>R<sup>2</sup> and HNR<sup>3</sup>R<sup>4</sup> wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are

as hereinbefore defined. This reaction is preferably performed in water at a pH above 7. Typically the reaction is performed at a temperature of 30 to 70°C and is usually complete in less than 24 hours. The compounds of formula  $\text{HNR}^1\text{R}^2$  and  $\text{HNR}^3\text{R}^4$  may be used as a mixture or added sequentially.

5 Many of the compounds of formula  $\text{HNR}^1\text{R}^2$  and  $\text{HNR}^3\text{R}^4$  are commercially available, for example ammonia and metanilic acid, others may be made easily by a skilled person using methods which are well known in the art.

10 The ratio of sulfo to sulfonamide substituents may be varied by varying the nature and amount of chlorinating agent used, the relative amounts of compounds of formula  $\text{HNR}^1\text{R}^2$  and  $\text{HNR}^3\text{R}^4$  used and the reaction conditions in both reactions.

When phthalocyanine tetrasulfonic acid is an intermediate in a route to compounds of Formula (1) it may be chlorinated by reacting with any suitable chlorinating agent.

15 Chlorination is preferably carried out by treating the phthalocyanine tetrasulfonic acid with chlorosulfonic acid preferably in the presence of an acid halide such as thionyl chloride, sulfuryl chloride, phosphorous pentachloride, phosphorous oxychloride and phosphorous trichloride.

M is preferably Cu.

In a first preferred embodiment  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  independently are H or methyl, more preferably  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are all H.

20 In the first preferred embodiment  $\text{R}^4$  is optionally substituted aryl, especially optionally substituted phenyl or naphthyl. More preferably  $\text{R}^4$  is optionally substituted phenyl, especially phenyl bearing at least one sulfo, carboxy or phosphato substituent and having further optional substituents. It is especially preferred that  $\text{R}^4$  is phenyl bearing a single sulfo, carboxy or phosphato substituent, particularly phenyl bearing a single sulfo substituent.

25 In a second preferred embodiment  $\text{R}^1$  and  $\text{R}^2$  independently are H or methyl, more preferably  $\text{R}^1$  and  $\text{R}^2$  are both H.

30 In the second preferred embodiment  $\text{R}^3$  and  $\text{R}^4$  together with the nitrogen atom to which they are attached represent an optionally substituted mono, bi or tricyclic aliphatic or aromatic ring. More preferably  $\text{R}^3$  and  $\text{R}^4$  together with the nitrogen atom to which they are attached represent an optionally substituted 3 to 8 membered aliphatic or aromatic ring. It is especially preferred that  $\text{R}^3$  and  $\text{R}^4$  together with the nitrogen atom to which they are attached represent an optionally substituted 5- or 6-membered aliphatic or aromatic ring. The optionally substituted aromatic or aliphatic ring formed by  $\text{R}^3$  and  $\text{R}^4$  together with the nitrogen atom to which they are attached may comprise at least one further hetero atom. Examples of preferred ring systems include imidazole, pyrazole, pyrrole, benzimidazole, indole, tetrahydro(iso)quinoline, decahydro(iso)quinoline, pyrrolidine, pyrroline, imidazolidine, imidazoline, pyrazolidine, pyrazoline, piperidine, piperazine, indoline, isoindoline, thiazolidine and morpholine.

Preferred optional substituents which may be present on  $R^1$ ,  $R^2$  and  $R^3$  (in the first preferred embodiment) are independently selected from: optionally substituted alkoxy (preferably  $C_{1-4}$ -alkoxy), optionally substituted aryl (preferably phenyl), optionally substituted aryloxy (preferably phenoxy), optionally substituted heterocyclic, polyalkylene oxide (preferably polyethylene oxide or polypropylene oxide), carboxy, phosphato, sulfo, nitro, cyano, halo, ureido,  $-SO_2F$ , hydroxy, ester,  $-NR^aR^b$ ,  $-COR^a$ ,  $-CONR^aR^b$ ,  $-NHCOR^a$ , carboxyester, sulfone, and  $-SO_2NR^aR^b$ , wherein  $R^a$  and  $R^b$  are each independently H or optionally substituted alkyl (especially  $C_{1-4}$ -alkyl). Optional substituents for any of the substituents described for  $R^1$ ,  $R^2$  and  $R^3$  may be selected from the same list of substituents.

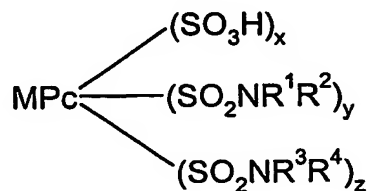
Preferred optional substituents which may be present on  $R^4$  in the first preferred embodiment or on the ring formed by  $R^3$  and  $R^4$  together with the nitrogen atom to which they are attached in the second preferred embodiment are independently selected from: optionally substituted alkyl (preferably  $C_{1-4}$ -alkyl), optionally substituted alkoxy (preferably  $C_{1-4}$ -alkoxy), optionally substituted aryl (preferably phenyl), optionally substituted aryloxy (preferably phenoxy), optionally substituted heterocyclic, polyalkylene oxide (preferably polyethylene oxide or polypropylene oxide), carboxy, phosphato, sulfo, nitro, cyano, halo, ureido,  $-SO_2F$ , hydroxy, ester,  $-NR^aR^b$ ,  $-COR^a$ ,  $-CONR^aR^b$ ,  $-NHCOR^a$ , carboxyester, sulfone, and  $-SO_2NR^aR^b$ , wherein  $R^a$  and  $R^b$  are each independently H or optionally substituted alkyl (especially  $C_{1-4}$ -alkyl). Optional substituents for any of the substituents described for  $R^4$  may be selected from the same list of substituents.

Preferably  $x$  has a value of 0.5 to 3.5.

Preferably  $y$  has a value of 0.5 to 3.5.

Preferably  $z$  has a value of 0.5 to 3.5.

Preferred compounds of Formula (1) are of Formula (2) and salts thereof:



Formula (2)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus;

$R^1$ ,  $R^2$  and  $R^3$  independently are H or optionally substituted  $C_{1-4}$ alkyl;

$R^4$  is phenyl bearing at least one sulfo, carboxy or phosphato substituent and having further optional substituents;

$x$  is 0.1 to 3.8;



y is 0.1 to 3.8;

z is 0.1 to 3.8;

the sum of (x+y+z) is 4; and the substituents, represented by x, y and z, are attached only to a  $\beta$ -position on the phthalocyanine ring.

Further optional substituents that may be present on R<sup>4</sup> in compounds of Formula (2) be independently selected from the list given above for R<sup>4</sup> in compounds of Formula (1).

The compounds of Formula (1) and Formula (2) are also preferably free from fibre reactive groups. The term fibre reactive group is well known in the art and is described for example in EP 0356014 A1. Fibre reactive groups are capable, under suitable conditions, of reacting with the hydroxyl groups present in cellulosic fibres or with the amino groups present in natural fibres to form a covalent linkage between the fibre and the dye. As examples of fibre reactive groups excluded from the compounds of Formula (1) there may be mentioned aliphatic sulfonyl groups which contain a sulfate ester group in beta-position to the sulfur atom, e.g. beta-sulfato-ethylsulfonyl groups, alpha, beta-unsaturated acyl radicals of aliphatic carboxylic acids, for example acrylic acid, alpha-chloro-acrylic acid, alpha-bromoacrylic acid, propiolic acid, maleic acid and mono- and dichloro maleic; also the acyl radicals of acids which contain a substituent which reacts with cellulose in the presence of an alkali, e.g. the radical of a halogenated aliphatic acid such as chloroacetic acid, beta-chloro and beta-bromopropionic acids and alpha, beta-dichloro- and dibromopropionic acids or radicals of vinylsulfonyl- or beta-chloroethylsulfonyl- or beta-sulfatoethyl-sulfonyl-endo- methylene cyclohexane carboxylic acids. Other examples of cellulose reactive groups are tetrafluorocyclobutyl carbonyl, trifluoro-cyclobutenyl carbonyl, tetrafluorocyclobutylethenyl carbonyl, trifluoro-cyclobutenylethenyl carbonyl; activated halogenated 1,3-dicyanobenzene radicals; and heterocyclic radicals which contain 1, 2 or 3 nitrogen atoms in the heterocyclic ring and at least one cellulose reactive substituent on a carbon atom of the ring, for example a triazinyl halide.

Acid or basic groups on the compounds of Formula (1) and Formula (2), particularly acid groups, are preferably in the form of a salt. Thus, the Formulae shown herein include the compounds in free acid and in salt form.

Preferred salts are alkali metal salts, especially lithium, sodium and potassium, ammonium and substituted ammonium salts (including quaternary amines such as ((CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>) and mixtures thereof. Especially preferred are salts with sodium, lithium, ammonia and volatile amines, more especially sodium salts. The compounds may be converted into a salt using known techniques.

The compounds of Formula (1) and Formula (2) may exist in tautomeric forms other than those shown in this specification. These tautomers are included within the scope of the present invention.

When the preferred route, as set out above, is used to synthesise compounds of Formula (1) and Formula (2) then they are predominantly formed as ammonium salts.

However, any known techniques may be used to exchange ammonia for another cation for example, acidification, optionally followed by dialysis, to remove the original cations with subsequent addition of alternative cations (e.g. by addition of alkali metal hydroxide, ammonium salt or amine). Use of ion exchange resins and reverse osmosis are other well-known techniques for cation exchange.

When the medium (b) comprises a mixture of water and organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C<sub>1-6</sub>-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C<sub>1-4</sub>-alkyl ethers of diols, preferably mono-C<sub>1-4</sub>-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic esters, preferably caprolactone; sulfoxides, preferably dimethyl sulfoxide and sulfolane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-miscible organic solvents.

Especially preferred water-miscible organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C<sub>1-4</sub>-alkyl and C<sub>1-4</sub>-alkyl ethers of diols, more preferably mono- C<sub>1-4</sub>-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

Examples of further suitable liquid media comprising a mixture of water and one or more organic solvents are described in US 4,963,189, US 4,703,113, US 4,626,284 and EP 4,251,50A.

When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50 to 125°C. The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore-described water-miscible organic

solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably  $\text{CH}_2\text{Cl}_2$ ; and ethers, preferably diethyl ether; and mixtures thereof.

When the liquid medium comprises a water-immiscible organic solvent, preferably a polar solvent is included because this enhances solubility of the compound in the liquid medium. Examples of polar solvents include  $\text{C}_{1-4}$ -alcohols.

In view of the foregoing preferences it is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) &/or an alcohol (especially a  $\text{C}_{1-4}$ -alkanol, more especially ethanol or propanol).

The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected that gives good control over the drying characteristics and storage stability of the ink.

Liquid media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

The liquid media may of course contain additional components conventionally used in ink-jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, fogging reducing additives and surfactants which may be ionic or non-ionic.

Although not usually necessary, further colorants may be added to the ink to modify the shade and performance properties. Examples of such colorants include C.I. Direct Yellow 86, 132, 142 and 173; C.I. Direct Blue 307; C.I. Food Black 2; C.I. Direct Black 168 and 195; C.I. Acid Yellow 23; and any of the dyes used in ink-jet printers sold by Seiko Epson Corporation, Hewlett Packard Company, Canon Inc. & Lexmark International.

It is preferred that the composition according to the invention is an ink suitable for use in an ink-jet printer. Ink suitable for use in an ink-jet printer is an ink which is able to repeatedly fire through an ink-jet printing head without causing blockage of the fine nozzles.

The inks may be incorporated in an ink-jet printer as a high concentration cyan ink, a low concentration cyan ink or both a high concentration and a low concentration ink. In the latter case this can lead to improvements in the resolution and quality of printed images. Thus the present invention also provides a composition (preferably an ink) where component (a) is present in an amount of 2.5 to 7 parts, more preferably 2.5 to 5 parts (a high concentration ink) or component (a) is present in an amount of 0.5 to 2.4 parts, more preferably 0.5 to 1.5 parts (a low concentration ink).

An ink suitable for use in an ink-jet printer preferably has a viscosity of less than 20 cP, more preferably less than 10 cP, especially less than 5 cP, at 25°C.

An ink suitable for use in an ink-jet printer preferably contains less than 500ppm, more preferably less than 250ppm, especially less than 100ppm, more especially less than 10ppm in total of divalent and trivalent metal ions (other than any divalent and trivalent metal ions bound to a colorant of Formula (1) or any other component of the ink).

5 Preferably an ink suitable for use in an ink-jet printer has been filtered through a filter having a mean pore size below  $10\mu\text{m}$ , more preferably below  $3\mu\text{m}$ , especially below  $2\mu\text{m}$ , more especially below  $1\mu\text{m}$ . This filtration removes particulate matter that could otherwise block the fine nozzles found in many ink-jet printers.

10 Preferably an ink suitable for use in an ink-jet printer contains less than 500ppm, more preferably less than 250ppm, especially less than 100ppm, more especially less than 10ppm in total of halide ions.

Preferred compositions comprise:

(a) from 0.01 to 30 parts of compounds of Formula (1); and

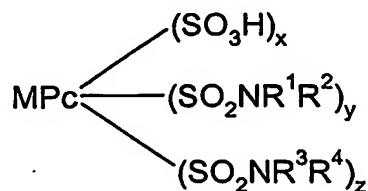
(b) from 70 to 99.99 parts of a liquid medium;

15 wherein all parts are by weight and the number of parts of (a)+(b)=100.

The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

20 Preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at  $20^\circ\text{C}$  of at least 10%. This allows the preparation of liquid dye concentrates that may be used to prepare more dilute inks and reduces the chance of the dye precipitating if evaporation of the liquid medium occurs during storage.

25 A second aspect of the present invention provides a compound of Formula (3): and salts thereof:



Formula (3)

30 wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus;

$\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  independently are H or optionally substituted  $\text{C}_{1-4}$ alkyl;

35  $\text{R}^4$  is phenyl bearing at least one sulfo, carboxy or phosphato substituent and having further optional substituents; or

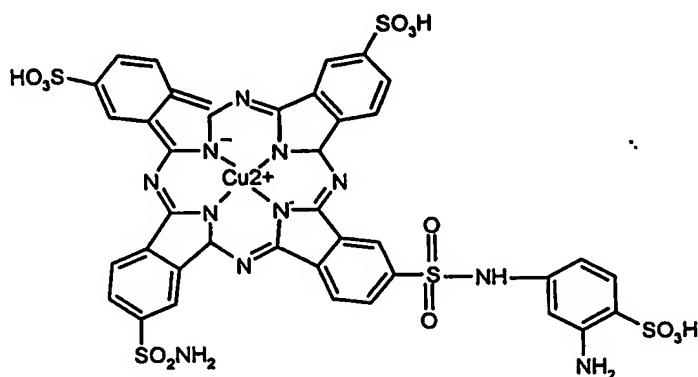
$R^3$  and  $R^4$  together with the nitrogen atom to which they are attached represent an optionally substituted 5- or 6-membered aliphatic or aromatic ring;

$x$  is 0.1 to 3.8;

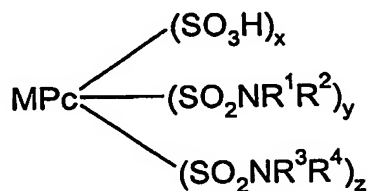
$y$  is 0.1 to 3.8;

$z$  is 0.1 to 3.8;

the sum of  $(x+y+z)$  is 4; and the substituents, represented by  $x$ ,  $y$  and  $z$ , are attached only to a  $\beta$ -position on the phthalocyanine ring; and provided that the compound of Formula (3) is not of formula



$M$ ,  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $x$ ,  $y$  and  $z$  are all as preferred in the first aspect of the invention. Preferred compounds of Formula (3) are of Formula (4) and salts thereof:



Formula (3)

wherein:

$M$  is Cu or Ni;

$Pc$  represents a phthalocyanine nucleus;

$R^1$ ,  $R^2$  and  $R^3$  independently are H or optionally substituted  $C_{1-4}$ alkyl;

$R^4$  is phenyl bearing at least one sulfo, carboxy or phosphato substituent and having further optional substituents;

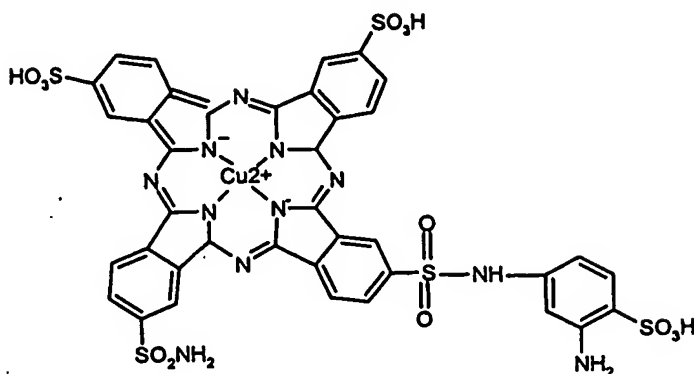
$x$  is 0.1 to 3.8;

$y$  is 0.1 to 3.8;

$z$  is 0.1 to 3.8;

the sum of  $(x+y+z)$  is 4; and the substituents, represented by  $x$ ,  $y$  and  $z$ , are attached only to a  $\beta$ -position on the phthalocyanine ring; and

provided that the compound of Formula (4) is not of formula



5 M, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, x, y and z in compounds of Formula (4) are all as preferred in the first aspect of the invention.

Preferably R<sup>4</sup> in Formula (4) is phenyl bearing a single sulfo substituent.

It is especially preferred that in compounds of Formula (4) R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are all H and R<sup>4</sup> is a single sulfo substituent meta to the bridging sulfonamide.

10 Further optional substituents for R<sup>4</sup> may be selected from the list of substituents preferred for R<sup>4</sup> above.

The compounds of Formula (3) and (4) have attractive, strong cyan shades and are valuable colorants for use in the preparation of ink-jet printing inks. They benefit from a good balance of solubility, storage stability and fastness to water and light

15 A third aspect of the invention provides a composition which comprises a compound of Formula (3) as defined in the second aspect of the invention and water.

It is preferred that the composition according to the third aspect of the invention is an ink suitable for use in an ink-jet printer.

20 The ink according to the third aspect of the invention may contain additional components conventionally used in ink-jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, kogation reducing additives and surfactants which may be ionic or non-ionic.

25 Although not usually necessary, further colorants may be added to the ink of the seventh aspect of the invention to modify the shade and performance properties. Examples of such colorants include C.I. Direct Yellow 86, 132, 142 and 173; C.I. Direct Blue 307; C.I. Food Black 2; C.I. Direct Black 168 and 195; C.I. Acid Yellow 23; and any of the dyes used in ink-jet printers sold by Seiko Epson Corporation, Hewlett Packard Company, Canon Inc. & Lexmark International.

30 A fourth aspect of the invention provides a process for forming an image on a substrate comprising applying an ink according to the first or third aspects of the invention thereto by means of an ink-jet printer.

The ink-jet printer preferably applies the ink to the substrate in the form of droplets that are ejected through a small orifice onto the substrate. Preferred ink-jet printers are piezoelectric ink-jet printers and thermal ink-jet printers. In thermal ink-jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected from the orifice in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink-jet printers the oscillation of a small crystal causes ejection of the ink from the orifice. Alternately the ink can be ejected by an electromechanical actuator connected to a moveable paddle or plunger, for example as described in International Patent Application WO00/48938 and International Patent Application WO00/55089.

The substrate is preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character. Glossy papers are especially preferred.

A fifth aspect of the present invention provides a material preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper more especially plain, coated or treated papers printed with a composition according to the first or third aspects of the invention, with a compound according to the third aspect of the invention or by means of a process according to the fourth aspect of the invention.

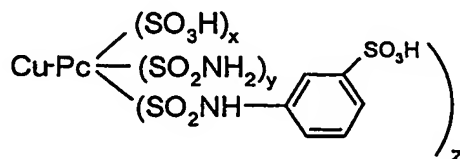
It is especially preferred that the printed material of the fifth aspect of the invention is a photograph printed using an ink-jet printer.

A sixth aspect of the present invention provides an ink-jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is as defined in the first or third aspects of the present invention. The cartridge may contain a high concentration ink and a low concentration ink, as described in the first aspect of the invention, in different chambers.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

#### Example 1

Preparation of the following dye substituted only in the  $\beta$ -position wherein x is 1.1, and (y + z) is 2.2:-



Analysis of compounds of Formula (1)

Conformation of the structure of compounds of Formula (1) is by mass spec. Elemental analysis is used to determine the ratios of x to y + z. Thus, when the sum of x plus y and z is not exactly 4 this is due to the presence of impurities. The presence of these impurities and their effect on the estimated values of x, y and z would be well known to a person skilled in the art who would appreciate that the value of x plus y plus z will not exceed 4 and who would treat the experimentally determined values of x, y and z as indicative of the true ratios of the groups.

Stage 1 - Preparation of copper phthalocyanine substituted with 4-SO<sub>3</sub>H groups in the  $\beta$ -position

The following components; potassium 4-sulfophthalic acid (56.8g), urea (120g), CuCl<sub>2</sub> (6.9g), ammonium molybdate (1.2g) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (7.5g) were mixed in a reaction vessel.

The mixture was then warmed in stages (130°C/30 minutes, 150°C/30 minutes, 180°C/30 minutes, 220°C) over 2 hours and the melt which formed was stirred at 220°C for a further 2 hours.

The solid which formed was extracted 4 times with hot water (4 x 200ml) and the extract was filtered to remove insoluble material.

The resultant filtrate was stirred at between 60°C – 70°C and then sufficient sodium chloride was added to give 7% brine solution. Stirring was continued and the solid which precipitated was filtered, washed with a 10% brine solution (200 ml) and pulled dry by vacuum. The resultant damp solid (77.6g) was slurried in acetone, filtered and dried first at room temperature and then at 50°C. Analysis revealed 3.8 sulfo groups per phthalocyanine.

Stage 2 Chlorosufonation of copper phthalocyanine substituted with 4-SO<sub>3</sub>H groups in the  $\beta$ -position

Phosphorous oxychloride (6.99g) was added to chlorosulfonic acid (69.9g) at 28°C. The sulfonated phthalocyanine product of stage 1 (11.8g) was then added to this mixture over 10-15 minutes while keeping temperature below 60°C. This reaction mixture was stirred at 50°C for 15-20 minutes and then slowly warmed to 120°C – 125°C and kept at this temperature, with stirring for 3 hours. At the end of this time the reaction mixture was cooled and stirred at room temperature overnight.

The next day the reaction-melt was drowned onto a mixture of water/ice/salt/HCl (50ml/150g/10g/2.5ml), keeping the temperature below 0°C using external cooling and



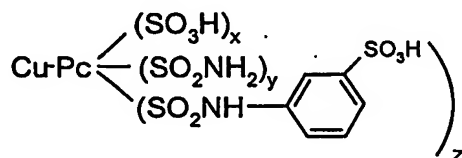
further addition of ice as necessary. The resultant suspension was stirred at 0°C for 30 minutes and then filtered, washed with acidified solution of ice cold 10% brine solution (100 ml) and pulled dry by vacuum to give the product as a damp paste.

### 5 Stage 3 Preparation of the title product

Damp paste prepared as in stage 2 (33g) was added in portions over 10-15 minutes at 0°-5°C to a stirred solution of metanilic acid (4.15g), concentrated ammonia (0.8g) and cold water (200ml). The resultant reaction mixture was stirred at 0° to 10°C for 10 30 minutes while keeping the pH above 8.5 by the addition of 2M NaOH. The mixture was allowed to warm up to room temperature over and stirred at pH 8.5 overnight. The mixture was then heated to 60° to 70°C, the pH was adjusted to 12 with 2M NaOH and stirred for 4 hours 30 minutes. The mixture was filtered and sodium chloride was added to the filtrate to give a 20% salt solution, the pH was then adjusted to less than pH 1 with 15 concentrated HCl. The solid which precipitated was filtered, washed with an acidified (i.e. less than pH 1) 20% solution of sodium chloride (200 ml) and pulled dry with a vacuum pump. The resultant damp paste was dissolved in deionised water at pH 8 and dialysed to low conductivity. The product was then filtered and dried at 70°C.

### 20 Example 2

Preparation of the following dye substituted only in the β-position wherein x is 1.5, and (y + z) is 3.4:



Stage 1 and 2 were carried out as in Example 1.

### 30 Stage 3 Preparation of the title product

The damp paste prepared in stage 2 (47g) was slurried in 200ml of cold (5°C) water. A solution of metanilic acid (8.65g) and concentrated ammonia (S.G. 0.88, 0.34ml) in 100 ml of water at pH 6.5 to 7 was added to this suspension of and stirred for 2 hours keeping the temperature below 10°C and maintaining the pH around 7 with 2M 35 NaOH solution. The mixture was then allowed to warm up to room temperature and stirred at pH 7.8 overnight. The next day the reaction mixture was warmed to 40°C and stirred at pH 7-8 for 2 hours. At the end of this time the reaction mixture was filtered and

and sodium chloride was added to the filtrate to give a 25% salt solution. The temperature was raised to 50° to 60°C and stirred and then the pH was adjusted to less than 1 with concentrated HCl, a further 5% sodium chloride was added and the precipitate which formed was collected by filtration pulled dry with a vacuum pump. This precipitate was dissolved in deionised water at pH 7 and dialysed to low conductivity. The product was then filtered and dried at 50°-60°C.

### Inks

Inks of the present invention may be prepared by dissolving 3.5g of the dye of Examples 1 or 2 in 100 ml of a liquid medium consisting of 2-pyrrolidone/thiodiglycol/Sufynol™ 465 in a weight ratio of 5:5:1.

### Further Inks

The inks described in Tables A and B may be prepared using the compounds made in Examples 1 and 2. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink-jet printing.

The following abbreviations are used in Table A and B:

PG = propylene glycol

DEG = diethylene glycol

NMP = N-methyl pyrrolidone

DMK = dimethylketone

IPA = isopropanol

MEOH = methanol

2P = 2-pyrrolidone

MIBK = methylisobutyl ketone

P12 = propane-1,2-diol

BDL = butane-2,3-diol

CET= cetyl ammonium bromide

PHO = Na<sub>2</sub>HPO<sub>4</sub> and

TBT = tertiary butanol

TDG = thiodiglycol

TABLE A

Example	Dye Content	Water	PG	DEG	NMP	DMK	NaOH	Na Stearate	IPA	MEOH	2P	MIBK
1	2.0	80	5		6	4					5	
2	3.0	90		5	5		0.2					
1	10.0	85	3		3	3				5	1	
2	2.1	91		8								1
1	3.1	86	5					0.2	4			5
2	1.1	81			9		0.5				9	
1	2.5	60	4	15	3	3			6	10	5	4
2	5	65		20					10			
1	2.4	75	5	4		5				6		5
2	4.1	80	3	5	2	10		0.3				
1	3.2	65		5	4	6			5	4	6	5
2	5.1	96								4		
1	10.8	90	5						5			
2	10.0	80	2	6	2	5					4	
1	1.8	80		5					1		15	
2	2.6	84			11						5	
1	3.3	80	2			10				2		6
2	12.0	90				7	0.3		3			
1	5.4	69	2	20	2	1					3	3
2	6.0	91			4						5	

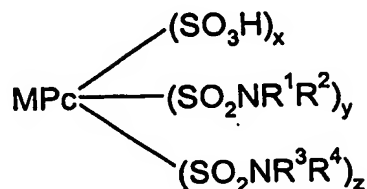
TABLE B

Example	Dye Content	Water	PG	DEG	NMP	CET	TBT	TDG	BDL	PHO	2P	P12
1	3.0	80	15			0.2						
2	9.0	90		5						1.2	5	5
1	1.5	85	5	5		0.15	5.0	0.2				
2	2.5	90		6	4					0.12		
1	3.1	82	4	8		0.3						
2	0.9	85		10					5	0.2		6
1	8.0	90		5	5			0.3				
2	4.0	70		10	4				1			
1	2.2	75	4	10	3				2		4	11
2	10.0	91			6						6	
1	9.0	76		9	7		3.0			0.95	3	
2	5.0	78	5	11							5	
1	5.4	86			7						6	
2	2.1	70	5	5	5						7	
1	2.0	90		10		0.1	0.2	0.1	5	0.1	5	
2	2	88										
1	5	78			5			10				
2	8	70	2		8			12			5	
1	10	80						15			5	
2	10	80		10				8			12	

CLAIMS

1. A composition comprising:

(a) a mixture of copper phthalocyanine dyes of Formula (1) and salts thereof:



Formula (1)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus;

R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> independently are H or optionally substituted C<sub>1-4</sub>alkyl;

R<sup>4</sup> is optionally substituted hydrocarbyl; or

R<sup>3</sup> and R<sup>4</sup> together with the nitrogen atom to which they are attached represent an optionally substituted aliphatic or aromatic ring system;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

the sum of (x+y+z) is 4; and

the substituents, represented by x, y and z, are attached only to a β-position on the phthalocyanine ring; and

(b) a medium which comprises water and an organic solvent or an organic solvent free from water.

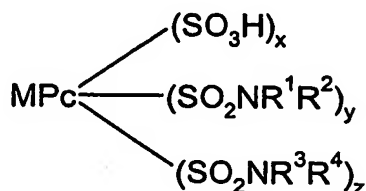
2. A composition according to claim 1 wherein R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> independently are H or methyl.

3. A composition according to either claim 1 or claim 2 wherein R<sup>4</sup> is optionally substituted aryl.

4. A composition according to any one of the preceding claims wherein R<sup>4</sup> is phenyl bearing at least one sulfo, carboxy or phosphato substituent and having further optional substituents.

5. A composition according to any one of the preceding claims wherein R<sup>4</sup> is phenyl bearing a single sulfo substituent.

6. A composition according to any one of the preceding claims wherein M is Cu.
7. A composition according to any one of the preceding claims wherein x is 0.5 to 3.5.
8. A composition according to any one of the preceding claims wherein y is 0.5 to 3.5.
9. A composition according to any one of the preceding claims wherein z is 0.5 to 3.5.
10. A compound of Formula (2) and salts thereof:



Formula (2)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus;

R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> independently are H or optionally substituted C<sub>1-4</sub>alkyl;

R<sup>4</sup> is phenyl bearing at least one sulfo, carboxy or phosphato substituent and having further optional substituents; or

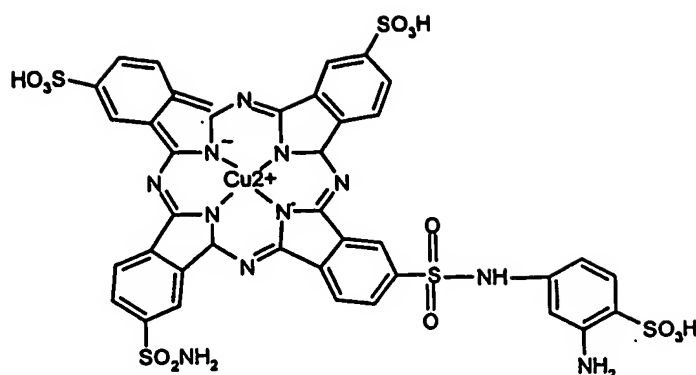
R<sup>3</sup> and R<sup>4</sup> together with the nitrogen atom to which they are attached represent an optionally substituted 5- or 6-membered aliphatic or aromatic ring;

x is 0.1 to 3.8;

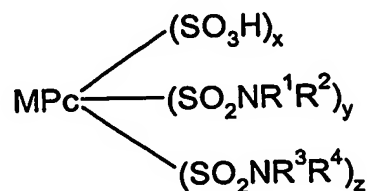
y is 0.1 to 3.8;

z is 0.1 to 3.8;

the sum of (x+y+z) is 4; and the substituents, represented by x, y and z, are attached only to a β-position on the phthalocyanine ring; and provided that the compound of Formula (2) is not of formula



11. A compound according to claim 10 of Formula (3) and salts thereof:



Formula (3)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus;

$\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  independently are H or optionally substituted  $\text{C}_{1-4}$ alkyl;

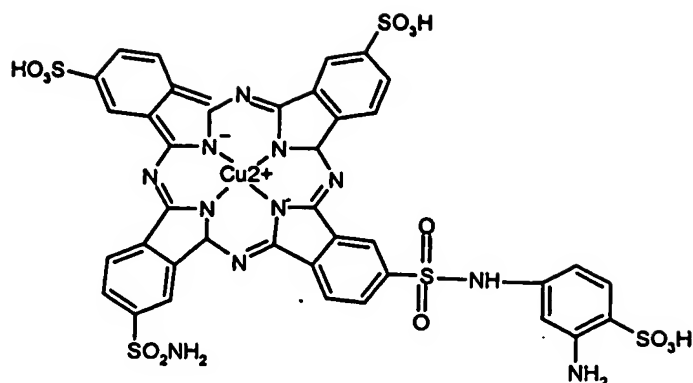
$\text{R}^4$  is phenyl bearing at least one sulfo, carboxy or phosphato substituent and having further optional substituents;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

the sum of  $(x+y+z)$  is 4; and the substituents, represented by x, y and z, are attached only to a  $\beta$ -position on the phthalocyanine ring; and provided that the compound of Formula (3) is not of formula



12. A compound according to either claim 10 or claim 11 wherein  $R^4$  is phenyl bearing a single sulfo substituent.

13. A compound according to any one of claims 10 to 12 wherein  $R^1$ ,  $R^2$  and  $R^3$  are all H and  $R^5$  is a single sulfo substituent meta to the bridging sulfonamide.

14. A composition which comprises a compound of Formula (2), as defined in any one of claims 10 to 13, and water.

15. A process for forming an image on a substrate comprising applying a composition according to any one of claims 1 to 9 or 13 thereto by means of an ink-jet printer.

16. A material printed with a composition according to any one of claims 1 to 9 or 14 or a compound according to any one of claims 10 to 13.

17. A material according to claim 16 which is a photograph printed using a process according to claim 15.

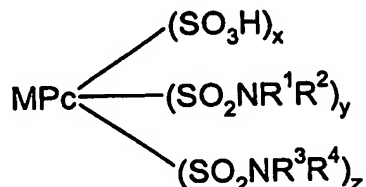
18. An ink-jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is as defined in any one of claims 1 to 9 or 14.



ABSTRACT  
COMPOUNDS, INKS AND PROCESSES

A composition comprising:

- 5 (a) a mixture of copper phthalocyanine dyes of Formula (1) and salts thereof:



Formula (1)

10 wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus;

R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> independently are H or optionally substituted C<sub>1-4</sub>alkyl;

R<sup>4</sup> is optionally substituted hydrocarbyl; or

15 R<sup>3</sup> and R<sup>4</sup> together with the nitrogen atom to which they are attached represent an optionally substituted aliphatic or aromatic ring system;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

20 the sum of (x+y+z) is 4; and

the substituents, represented by x, y and z, are attached only to a β-position on the phthalocyanine ring; and

(b) a medium which comprises water and an organic solvent or an organic solvent free from water. Also novel compounds, ink-jet printing processes, printed images, and  
25 cartridges.

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